This invention relates to the field of hydrocracking hydrocarbon-containing feedstocks for the purpose of producing middle distillates, and more particularly gas oil.

The hydrocracking of heavy petroleum fractions is a very important refining process that makes it possible to produce lighter fractions from excess heavy feedstocks that cannot be readily upgraded. In some cases, these processes can also produce a highly purified residue that can provide excellent bases for oils.

Certain hydrocracking processes, often described as "once through" processes, comprise a preliminary hydrotreatment stage with a limited conversion of light fractions, making it possible to transform the nitrogen-containing and sulfur-containing organic compounds. These types of processes generally do not comprise an intermediate separation between hydrotreatment and hydrocracking.

Other hydrocracking processes comprise a preliminary hydrorefining stage that makes it possible to convert between 20 and 60% of the feedstock, a stage of separation for recovering unconverted products, and a hydrocracking stage. These processes are often described as two-stage processes.

International Patent Application WO 99/47625 describes a process for converting a hydrocarbon feedstock into a product that has a lower mean molecular weight. This process comprises a hydrocracking stage that is used with a catalyst based on a cracking component and a hydrogenation component, whereby the latter comprises palladium and platinum in a molar ratio that varies between 10:1 and 1:10.

The implementation of such a process generally involves the use of a hydrocracking catalyst that comprises a zeolite, which makes it possible to produce gases,

gasolines and middle distillates with high conversion levels, but contrary to a mediocre selectivity of middle distillates.

A process was found for the production of middle distillates that makes it possible to reconcile a strong conversion with a high selectivity level of middle distillates under operating conditions that are favorable to an increase in the cycle time of catalysts and to the production of gas oils and kerosene of excellent quality.

A gas oil of excellent quality is defined as a gas oil that has:

- a sulfur content that is less than 50 ppm, preferably less than 30 ppm, and more preferably less than 10 ppm,
- a cetane number that is higher than 51, preferably higher than 55,
- a content of polyaromatic compounds that is less than 11% by weight, preferably less than 5% by weight, and more preferably less than 2% by weight, and
- a content of aromatic compounds that is less than 15% by weight, preferably less than 10% by weight.

A kerosene of excellent quality is defined as a kerosene whose smoke point is higher than 20 mm, preferably higher than 25 mm.

This invention therefore relates to a hydrocracking process for the conversion of a hydrocarbon feedstock that comprises:

- a hydrorefining stage in which the feedstock is brought into contact with the hydrogen in the presence of a hydrorefining catalyst, at a temperature T1, and an effluent that comprises converted products and unconverted products is recovered,

- optionally a separation stage in which at least a portion of the converted products formed during the hydrorefining stage and a fraction that comprises the unconverted products are separated, and
- a hydrocracking stage, in which the unconverted products (therefore optionally at least a portion of the fraction that contains said products that are obtained from the separation) are, at least in part, brought into contact with the hydrogen, in the presence of an amorphous hydrocracking catalyst that comprises a substrate, palladium and platinum, at a temperature T2 that is less than T1, whereby the difference between T1 and T2 is between 5 and 50°C, preferably between 10 and 40°C, and more preferably between 15 and 30°C.

Very varied feedstocks can be treated by the process of the invention. Generally, these feedstocks contain at least 20% by volume, and often at least 80% by volume, of compounds that have a boiling point above 340°C.

Preferably, 95% of the compounds that are present in the feedstock have a boiling point of higher than 340°C, and more preferably, 95% of the compounds that are present in the feedstock have a boiling point that is higher than 370°C.

The nitrogen content of the treated hydrocarbon-containing feedstocks in the process according to the invention is generally higher than 500 ppm by weight, preferably between 500 and 5,000 ppm by weight, more preferably between 700 and 4,000 ppm by weight, and even more preferably between 1,000 and 3,000 ppm by weight.

The sulfur content of these hydrocarbon-containing feedstocks is preferably between 0.01 and 5% by weight, and more preferably between 0.2 and 4% by weight.

According to the process of the invention, the feedstock is subjected, in a first reaction zone, to at least one hydrorefining stage, during which it is brought into contact with the hydrogen in the presence of a hydrorefining catalyst. During this hydrorefining stage, the feedstock generally undergoes hydrodesulfurization, hydrodenitration, as well as a conversion of a portion of the latter into conversion products such as gases, gasolines and middle distillates.

The hydrorefining catalysts can be selected from among the catalysts that are commonly used in this field.

The hydrorefining catalyst can preferably comprise a matrix, at least one hydro-dehydrogenating element that is selected from the group that is formed by the elements of group VIB and group VIII of the periodic table.

The matrix can consist of compounds that are used alone or in a mixture, such as alumina, halogenated alumina, silica, silica-alumina, clays (selected from, for example, natural clays such as kaolin or bentonite), magnesia, titanium oxide, boron oxide, zirconia, aluminum phosphates, titanium phosphates, zirconium phosphates, carbon, and aluminates. It is preferred to use matrices that contain alumina, in all of these forms that are known to one skilled in the art, and even more preferably aluminas, for example gamma-alumina.

The hydro-dehydrogenating element can be selected from the group that is formed by the elements of group VIB and non-noble element of group VIII of the periodic table. The hydro-dehydrogenating element is preferably selected from the group that is formed by molybdenum, tungsten, nickel and cobalt. More preferably, the hydro-dehydrogenating element comprises at least one element of group VIB and at least one

non-noble element of group VIII. This hydro-dehydrogenating element can comprise, for example, a combination of at least one element of group VIII (Ni, Co) with at least one element of group VIB (Mo, W).

The hydrorefining catalyst preferably also comprises at least one dopant that is deposited on said catalyst and is selected from the group that is formed by phosphorus, boron and silicon. In particular, the hydrorefining catalyst can comprise, as dopants, boron and/or silicon, with optionally, in addition, phosphorus. The contents of boron, silicon and phosphorus are generally between 0.1 and 20%, preferably 0.1 and 15%, and more preferably between 0.1-10%.

The hydrorefining catalyst can advantageously comprise phosphorus. This compound provides, i.a., two main advantages to the hydrorefining catalyst, whereby a first advantage is a greater facility of preparation of said catalyst during in particular the impregnation of the hydro-dehydrogenating element, for example from solutions based on nickel and molybdenum. A second advantage provided by this compound is an increase in the hydrogenation activity of the catalyst.

The hydrorefining catalyst can also comprise at least one element of the group VIIA (chlorine and fluorine are preferred) and/or at least one element of group VIIB (manganese is preferred), and optionally at least one element of group VB (niobium is preferred).

In a preferred hydrorefining catalyst, the total concentration of metal oxides of groups VIB and VIII is between 5 and 40% by weight, preferably between 7 and 30% by weight, and the ratio by weight that is expressed in terms of metal oxide between group VIB metal (or metals) vs. group VIII metal (or metals) is between 20 and 1.25, preferably

between 10 and 2. The concentration of phosphorus oxide P_2O_5 can be less than 15% by weight, preferably less than 10% by weight.

In another hydrorefining catalyst that comprises boron and/or silicon, preferably boron and silicon, said catalyst generally comprises, in % by weight relative to the total mass of said catalyst,

- from 1 to 99%, preferably from 10 to 98%, and more preferably from 15 to 95% of at least one matrix,
- from 3 to 60%, preferably from 3 to 45%, and more preferably from 3 to 30% of at least one metal of group VIB,
- optionally from 0 to 30%, preferably from 0 to 25%, and more preferably from 0 to 20% of at least one metal of group VIII,
- from 0.1 to 20%, preferably from 0.1 to 15%, and more preferably
- from 0.1 to 10% of boron and/or 0.1 to 20%, preferably from 0.1 to 15%, and more preferably from 0.1 to 10% of silicon,
- optionally from 0 to 20%, preferably from 0.1 to 15%, and more preferably from 0.1 to 10% of phosphorus, and
- optionally from 0 to 20%, preferably from 0.1 to 15%, and more preferably from 0.1 to 10% of at least one element that is selected from group VIIA, for example fluorine.

In another hydrorefining catalyst, said catalyst comprises:

- between 1 and 95% by weight (% oxide) of at least one matrix, preferably alumina,

- between 5 and 40% by weight (% oxide) of at least one non-noble element of groups VIB and VIII,
- between 0 and 20%, preferably between 0.1 and 20% by weight (% oxide) of at least one promoter element that is selected from among phosphorus, boron, and silicon,
- between 0 and 20% by weight (% oxide) of at least one element of group VIIB (manganese, for example),
- between 0 and 20% by weight (% oxide) of at least one element of group VIIA (fluorine, chlorine, for example), and
- between 0 and 60% by weight (% oxide) of at least one element of group VB (niobium, for example).

In a general way, hydrorefining catalysts that have the following atomic ratios are preferred:

- an atomic ratio of group VIII metals/group VIB metals ranging from 0 to 1,
- an atomic ratio of B/group VIB metals ranging from 0.01 to 3,
- an atomic ratio of Si/group VIB metals ranging from 0.01 to 1.5,
- an atomic ratio of P/group VIB metals ranging from 0.01 to 1, and
- an atomic ratio of group VIIA elements/group VIB metals ranging from 0.01 to 2.

The particularly preferred hydrorefining catalysts are the NiMo and/or NiW catalysts on alumina, also the NiMo and/or NiW catalysts on alumina that is doped with at least one element that is included in the group of atoms formed by phosphorus, boron, silicon and fluorine.

The hydrorefining catalysts that are described above are therefore used during the hydrorefining stage, often called a hydrotreatment stage.

The hydrorefining catalyst is preferably subjected in advance to a sulfurization treatment that makes it possible to transform, at least in part, the metal sulfide radicals before contact with the feedstock to be treated. This treatment of activation by sulfurization is well known to one skilled in the art and can be carried out by any method that is already described in the literature or in–situ, i.e., in the reactor, or ex-situ.

The operating conditions that are used during the hydrorefining stage preferably can be defined as follows:

- a temperature T1 ranging from 330 to 420°C, preferably from 350 to 410°C, more preferably from 360 to 400°C, and even more preferably from 370 to 390°C;
- a pressure that is higher than 7.5 MPa, preferably higher than 8.2 MPa, more preferably higher than 9.0 MPa, and even more preferably higher than 11.0 MPa and less than 20 MPa;
- a volumetric flow rate ranging from 0.1 to 6 h^{-1}, preferably from 0.2 to 3 h^{-1};
- an amount of hydrogen that is introduced with a volumetric ratio of liter of hydrogen by liter of hydrocarbons ranging from 100 and 2,000 l/l.

During the hydrorefining stage of the process of the invention, the contents of organic nitrogen-containing compounds, organic sulfur-containing compounds and condensed polycyclic aromatic hydrocarbons are generally reduced. A large portion of the nitrogen-containing and sulfur-containing organic products of the feedstock is found transformed into H2S and NH3.

The operating conditions of the hydrorefining stage are preferably established such that the organic nitrogen content of the feedstock that is obtained from this hydrorefining is less than 10 ppm by weight, preferably less than 5 ppm.

The operating conditions of the hydrorefining stage are preferably established so as to obtain a level of conversion of the feedstock into compounds whose boiling point is less than 340°C or, even better, less than 370°C, encompassed between 10 and 50%, preferably between 20 and 40%.

According to the process of this invention, the effluent that is recovered during the hydrorefining stage is subjected to a separation stage in which at least a portion of the converted products formed during the hydrorefining stage and a fraction that comprises the unconverted products are separated.

The effluent of this hydrorefining stage can be sent into a separation means, such as, for example, a separator tank, so as to eliminate the ammonia and the hydrogen sulfide that are produced during the hydrorefining stage. The hydrocarbon-containing effluent, obtained from this separation, can undergo an atmospheric distillation. This distillation can be complemented, in some cases, by a vacuum distillation. The purpose of the distillation is to carry out the separation between the converted products, i.e., generally having boiling points of less than 340°C, preferably less than 370°C, and a fraction, generally liquid, that comprises unconverted products.

It is advantageously possible to distill at atmospheric pressure to obtain several converted products, such as, for example, gasolines, kerosene, and gas oil, as well as unconverted products that have an initial boiling point of higher than 340°C or else higher than 370°C.

According to the process of this invention, the fraction that comprises the unconverted products is, at least in part, subjected to a hydrocracking stage.

The fraction that is subjected to a hydrocracking stage preferably essentially consists of products that have a boiling point that is higher than 340°C, preferably higher than 370°C.

This fraction that is subjected to the hydrocracking stage generally has very low contents of organic sulfur, organic nitrogen, hydrogen sulfide and ammonia. Organic sulfur and organic nitrogen are defined as the sulfur and the nitrogen that are included in organic compounds.

The organic nitrogen content of the portion of the fraction that comprises the unconverted products subjected to the hydrocracking stage is preferably less than 10 ppm by weight, more preferably less than 5 ppm by weight.

The organic sulfur content of the portion of the fraction that comprises the unconverted products subjected to the hydrocracking stage is preferably less than 100 ppm by weight, more preferably less than 20 ppm by weight.

The H_2S content of the portion of the fraction that comprises the unconverted products subjected to the hydrocracking stage is preferably less than 100 ppm by weight, more preferably less than 10 ppm by weight, and even more preferably less than 5 ppm by weight.

The NH_3 content of the portion of the fraction that comprises the unconverted products subjected to the hydrocracking stage is preferably less than 100 ppm by weight, more preferably less than 10 ppm by weight and even more preferably less than 5 ppm by weight.

According to the process of the invention, the hydrocracking stage is carried out by contact with hydrogen in the presence of a hydrocracking catalyst.

The hydrogen that is used during the hydrocracking stage generally has a hydrogen sulfide content of less than 100 ppm, preferably less than 10 ppm, more preferably less than 5 ppm, and an ammonia content that is less than 50 ppm, preferably less than 10 ppm, more preferably less than 5 ppm.

According to the process of the invention, the hydrocracking catalyst exhibits an amorphous or non-zeolitic nature. The hydrocracking catalyst generally comprises at least one amorphous acidic substrate and at least one noble metal-type hydro-dehydrogenating function.

The substrates generally have large surface areas that can range from 150 to 800 m^2g^{-1} and exhibit a surface acidity. They can be selected from among the halogenated aluminas (in particular chlorinated or fluorinated aluminas), the boron and aluminum oxide combinations, the titanium, silicon and aluminum oxide combinations, the zirconium, aluminum and silicon oxide combinations, the amorphous silica-aluminas, and the halogenated silica-aluminas (chlorinated or fluorinated silica-aluminas in particular). These oxides or combinations of amorphous oxides can be obtained by any methods of synthesis that are known to one skilled in the art. Preferably, the substrate of the hydrocracking catalyst is an amorphous silica-alumina.

The substrate can consist of pure silica-alumina or result from the mixing, with said silica-alumina, of a binder such as silica (SiO2), alumina (Al2O3), clays, titanium oxide (TiO2), boron oxide (B2O3) and zirconia (ZrO2) and any mixture with the binders cited above. The preferred binders are silica and alumina and, even more preferably,

alumina in all of these forms that are known to one skilled in the art, for example gamma-alumina. The content by weight of binder in the substrate of the catalyst can be between 0 and 40% by weight, preferably between 1 and 40% by weight, and more preferably between 5% and 20% by weight. This has the result that the content by weight of silica-alumina is generally between 60-100% by weight. However, the catalysts whose substrate consists only of silica-alumina without any binder are preferred.

The substrate can be prepared by shaping silica-alumina with or without the presence of binder by any technique that is known to one skilled in the art. The shaping can be carried out by, for example, extrusion, pelletizing, the drop (oil-drop) coagulation method, turntable granulation or any other method that is well known to one skilled in the art. At least one calcination can be carried out after any of the stages of the preparation; it is usually carried out in air at a temperature of at least 150°C, preferably at least 300°C.

The catalyst substrates can exhibit a certain number of characteristics.

Among the characteristics that are used below, the B.E.T. specific surface area is determined by adsorption of nitrogen according to ASTM Standard D3663-78 established from the BRUNAUER-EMMETT-TELLER method described in the periodical "The Journal of American Society," 60, 309 (1938).

Relative to the measurements of volumes, they are generally carried out by mercury porosimeter intrusion according to ASTM Standard D4284-83 at a maximum pressure of 4,000 bar, using a surface tension of 484 dyne/cm and a contact angle for the amorphous silica-alumina substrates of 140°. The mercury mean diameter, D_{mean}, is defined as being a diameter such that all the pores of a size smaller than this diameter constitute 50% of the pore volume (VHg) in an interval of between 36 Å and 1,000 Å.

So as to obtain better precision, the value of the mercury volume in ml/g that is provided in the text below corresponds to the value of the total mercury volume in ml/g that is measured in the sample less the value of the mercury volume in ml/g that is measured in the same sample for a pressure that corresponds to 30 psi (about 2 bar). So as to better characterize the pore distribution, the following mercury pore distribution criteria are defined: volume V1 corresponds to the volume that is contained in the pores whose diameter is less than the mean diameter less 30 Å. Volume V2 corresponds to the volume that is contained in the pores with a diameter that is larger than the mean diameter less 30 Å and less than the mean diameter plus 30 Å. Volume V3 corresponds to the volume that is contained in the pores with a diameter that is larger than the mean diameter plus 30 Å. Volume V4 corresponds to the volume that is contained in the pores whose diameter is less than the mean diameter less 15 Å. Volume V5 corresponds to the volume that is contained in the pores with a diameter that is larger than the mean diameter less 15 Å and less than the mean diameter plus 15 Å. Volume V6 corresponds to the volume that is contained in the pores with a diameter that is larger than the mean diameter plus 15 Å.

Below, the pore distribution that was measured by nitrogen adsorption was determined by the Barrett-Joyner-Halenda (BJH) model. The nitrogen adsorption-desorption isotherm according to the BJH model is described in the periodical "The Journal of American Society," 73, 373 (1951) written by E. P. Barrett, L. G. Joyner and P. P. Halenda. In the following presentation of the invention, nitrogen adsorption volume is defined as the volume that is measured for P/PO = 0.99, pressure for which it is accepted that nitrogen has filled all the pores. The nitrogen desorption mean diameter is

defined as being a diameter such that all the pores that are smaller than this diameter constitute 50% of pore volume (Vp) measured on the desorption branch of the nitrogen isotherm. Adsorption surface area is defined as the surface area that is measured on the branch of the adsorption isotherm. Reference will be made to, for example, the article of A. Lecloux, "Mémoires Société Royale des Sciences de Liège, 6th Series, Part I, Volume 4, pp. 169-209 (1971)."

The sodium content has been measured by atomic absorption spectrometry.

In the following presentation, the x-ray analysis is carried out on powder with a Philips PW 1830 diffractometer that operates by reflection and is equipped with a rear monochromator by using the CoKalpha radiation ($\lambda K_{a1} = 1.7890$ Å, $\lambda\ K_{a2} = 1.793$ Å, intensity ratio $K_{a1}/K_{a2} = 0.5$). For the X diffraction diagram of the gamma-alumina, reference will be made to the ICDD data base, form 10-0425. In particular, the two most intense peaks are located at a position that corresponds to one d encompassed between 1.39 and 1.40 Å and one d encompassed between 1.97 Å to 2.00 Å. d is called the interreticular distance that is derived from the angular position by using Bragg's equation ($2\ d_{(hkl)} * \sin(\theta) = \eta * \lambda$). Gamma-alumina is defined in the text below, i.a., as, for example, an alumina contained in the group that consists of cubic gamma-aluminas, pseudo-cubic gamma-aluminas, tetragonal gamma-aluminas, poorly or slightly crystallized gamma-aluminas, large-surface-area gamma-aluminas, low-surface-area gamma-aluminas, gamma-aluminas that are obtained from coarse boehmite, gamma-aluminas that are obtained from crystallized boehmite, gamma-aluminas that are obtained from boehmite that is slightly or poorly crystallized, gamma-aluminas that are obtained from a mixture of crystallized boehmite and an amorphous gel, gamma-aluminas that are

obtained from an amorphous gel, and gamma-aluminas evolving toward delta-aluminas. For the positions of diffraction peaks of eta-, delta- and theta-aluminas, it is possible to refer to the article by B. C. Lippens and J. J. Steggerda in Physical and Chemical Aspects of Adsorbents and Catalysts, E. G. Linsen (Ed.), Academic Press, London. 1970, pp. 171-211.

Finally, in the following presentation, the analyses by RMS MAS are carried out on a spectrometer of the Brüker Company such as MSL 400, with a 4 mm probe. The speed of rotation of the samples is on the order of 11 kHz. Potentially, the NMR of the aluminum makes it possible to distinguish three types of aluminum whose chemical displacements are presented below:

- between 100 and 40 ppm, tetra-coordinated-type aluminum, denoted as Al_{IV},
- between 40 and 20 ppm, penta-coordinated-type aluminum, denoted as Al_{V},
- between 20 and –100 ppm, hexa-coordinated-type aluminum, denoted as Al_{VI}.

The aluminum atom is a quadripolar core. Under certain analysis conditions (weak radiofrequency fields: 30 kHz, low-impulse angle: $\pi/2$ and water-saturated sample), the NMR technique of magic angle rotation (MAS) is a quantitative technique. The decomposition of the NMR MAS spectra makes it possible to gain access directly to the amount of different radicals. The spectrum is locked in chemical displacement relative to a 1 M solution of aluminum nitrate. The aluminum signal is at zero ppm. We chose to integrate the signals between 100 and 20 ppm for the Al_{IV} and Al_{V}, which

corresponds to area 1, and between 20 and –100 ppm for Al_{VI}, which corresponds to area 2. In the following presentation of the invention, proportion of octahedral Al_{VI} is defined as the following ratio: area 2/(area 1 + area 2).

The packing density (DRT) of the substrates and catalysts that can be used in the process according to the invention is measured in the manner that is described in the work "Applied Heterogeneous Catalysis" by J. F. Le Page, J. Cosyns, P. Courty, E. Freund, J.-P. Franck, Y. Jacquin, B. Juguin, C. Marcilly, G. Martino, J. Miguel, R. Montarnal, A. Sugier, H. Van Landeghem, Technip. Paris, 1987. A graduated cylinder with acceptable dimensions is filled with catalyst by successive additions; and between each addition, the catalyst is packed by shaking the cylinder until a constant volume is achieved. This measurement is generally carried out on 1,000 cm^3 of catalyst that is packed into a cylinder whose height to diameter ratio is close to 5:1. This measurement can preferably be made on automated devices such as Autotap® that is marketed by Quantachrome®.

The acidity of the catalyst substrate that can be used in the process according to the invention is measured by infra-red (IR) spectrometry. The IR spectra are recorded on a Nicolet interferometer such as Nexus-670 under a resolution of 4 cm^{-1} with a Happ-Genzel-type apodization. The sample (20 mg) is pressed in the form of a self-supported pellet, then is placed in an in-situ analysis cell (25°C to 550°C, furnace offset from the IR beam, secondary vacuum of 10^{-6} mbar). The diameter of the pellet is 16 mm.

The sample is pretreated in the following way to eliminate the physisorbed water and to dehydroxylate partially the surface of the catalyst to obtain a representative image of the acidity of the catalyst in use:

- increase in temperature from 25°C to 300°C in 3 hours
- plateau of 10 hours at 300°C
- drop in temperature from 300°C to 25°C in 3 hours.

The basic probe (pyridine) is then adsorbed with saturating pressure at 25°C and then thermo-desorbed according to the following plateaus:

- 25°C for 2 hours under secondary vacuum
- 100°C for 1 hour under secondary vacuum
- 200°C for 1 hour under secondary vacuum
- 300°C for 1 hour under secondary vacuum.

A spectrum is recorded at 25°C at the end of the pretreatment and at each desorption plateau in transmission mode with an accumulation time of 100 s. The spectra are set to iso-mass (i.e., assumed to be at iso-thickness) (20 mg exactly). The number of Lewis sites is proportional to the surface area of the peak whose maximum lies around 1450 cm^{-1}, including any shoulder. The number of Bronsted sites is proportional to the surface area of the peak whose maximum is located toward 1545 cm^{-1}. The ratio of the number of Bronsted sites/number of Lewis sites is estimated to be equal to the ratio of the surface areas of two peaks described above. The surface area of peaks at 25°C is generally used. This B/L ratio is generally calculated from the spectrum that is recorded at 25°C at the end of the pretreatment.

According to a first embodiment of this invention, the substrate of the hydrocracking catalyst is a non-zeolitic substrate with a silica-alumina base (i.e., that comprises silica and alumina) that comprises the following characteristics:

- a content by mass of silica (SiO_2) that is more than 5% by weight and less than or equal to 95% by weight, preferably between 10 and 80% by weight, preferably a silica content that is more than 20% by weight and less than 80% by weight, and even more preferably more than 25% by weight and less than 75% by weight, and the silica content is advantageously encompassed between 10 and 50% by weight,
- preferably a cationic impurity content that is less than 0.1% by weight, preferably less than 0.05% by weight, and even more preferably less than 0.025% by weight. Cationic impurity content is defined as the total alkaline content.
- preferably an anionic impurity content that is less than 1% by weight, preferably less than 0.5% by weight, and even more preferably less than 0.1% by weight.
- a mean pore diameter, measured by mercury porosimetry, encompassed between 20 and 140 Å, preferably between 40 and 120 Å, and even more preferably between 50 and 100 Å,
- preferably a ratio between volume V2, measured by mercury porosimetry, encompassed between D_{mean} - 30 Å and D_{mean} + 30 Å, to the total pore volume that is also measured by mercury porosimetry, that is more than 0.6, preferably more than 0.7, and even more preferably more than 0.8,
- preferably a volume V3 that is encompassed in the pores with a diameter of more than D_{mean} + 30 Å, measured by mercury porosimetry, that is less than 0.1 ml/g, preferably less than 0.06 ml/g, and even more preferably less than 0.04 ml/g,
- preferably a ratio between volume V5 that is encompassed between D_{mean} - 15 Å and D_{mean} + 15 Å, measured by mercury porosimetry, and volume V2 that is encompassed between D_{mean} - 30 Å and D_{mean} + 30 Å, measured by mercury

porosimetry, that is more than 0.6, preferably more than 0.7, and even more preferably more than 0.8,

- preferably a volume V6 that is encompassed in the pores with a diameter of more than D_{mean} + 15 Å, measured by mercury porosimetry, that is less than 0.2 ml/g, preferably less than 0.1 ml/g, and even more preferably less than 0.05 ml/g,
- a total pore volume, measured by mercury porosimetry, encompassed between 0.1 ml/g and 0.6 ml/g, preferably encompassed between 0.20 and 0.50 ml/g, and even more preferably more than 0.20 ml/g,
- a total pore volume, measured by nitrogen porosimetry, encompassed between 0.1 ml/g and 0.6 ml/g, preferably between 0.20 and 0.50 ml/g,
- a BET specific surface area encompassed between 100 and 550 m^2/g, preferably encompassed between 150 and 500 m^2/g,
- preferably an adsorption surface area such that the ratio between the adsorption surface area and the BET surface area is more than 0.5, preferably more than 0.65, and more preferably more than 0.8,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 140Å, of less than 0.1 ml/g, preferably of less than 0.05 ml/g, and even more preferably of less than 0.03 ml/g,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 160 Å, of less than 0.1 ml/g, preferably of less than 0.05 ml/g, and even more preferably of less than 0.025 ml/g,

- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 200 Å, of less than 0.1 ml/g, preferably of less than 0.05 ml/g, and even more preferably of less than 0.025 ml/g,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 500 Å, of less than 0.01 ml/g,
- an X diffraction diagram that contains at least the main lines that are characteristic of at least one of the transition aluminas contained in the group that consists of the rho, chi, kappa, eta, gamma, theta and delta aluminas, and preferably characterized in that it contains at least the main lines that are characteristic of at least one of the transition aluminas contained in the group that consists of the gamma, eta, theta and delta alumina, and more preferably, characterized in that it contains at least the main lines that are characteristic of the gamma–alumina and eta-alumina, and even more preferably characterized in that it contains the peaks at one d encompassed between 1.39 and 1.40 Å and the peaks at one d encompassed between 1.97 Å and 2.00 Å .

The NMR MAS spectra of the solid of ^{27}Al of such a substrate show two clusters of separate peaks. A first type of aluminum whose maximum resonates toward 10 ppm extends between –100 and 20 ppm. The position of the maximum suggests that these radicals are essentially of Al_{VI} type (octahedral). A second type of minority aluminum whose maximum resonates toward 60 ppm extends between 20 and 110 ppm. This cluster can be decomposed into at least two radicals. The predominant radical of this cluster would correspond to Al_{IV} atoms (tetrahedral). For the substrates of this

embodiment of the invention, advantageously the proportion of octahedral Al_{VI} is more than 50%, preferably more than 60%, and even more preferably more than 70%.

The substrate can comprise at least two silico-aluminum zones, whereby said zones have Si/Al ratios that are less than or greater than the overall Si/Al ratio that is determined by X fluorescence. A substrate that has an overall Si/Al ratio that is equal to 0.5 thus comprises, for example, two silico-aluminum zones: one of the zones has an Si/Al ratio that is determined by MET of less than 0.5, and the other zone has an Si/Al ratio that is determined by MET of between 0.5 and 2.5.

The substrate can comprise a single silico-aluminum zone, whereby said zone has an Si/Al ratio that is equal to the overall Si/Al ratio that is determined by X fluorescence and is less than 2.3.

The acidity of the catalyst substrate that can be used in the process according to the invention can advantageously be measured, without restricting the scope of the invention, by IR tracking of the thermodesorption of the pyridine. Generally, the B/L ratio, as described above, of the substrate according to the invention is between 0.05 and 1, preferably between 0.05 and 0.7, very preferably between 0.06 and 0.3, and even more preferably between 0.075 and 0.15.

The packing density of the substrates, after calcination, is generally more than 0.65 g/cm^3, preferably more than 0.72 g/cm^3, very preferably more than 0.75 g/cm^3, and even more preferably more than 0.78 g/cm^3.

The packing density of the catalysts that are obtained from this substrate is generally more than 0.85 g/cm^3, preferably more than 0.95 g/cm^3, very preferably more than 1.025 cm^3/g, and even more preferably more than 1.1 g/cm^3.

More specifically, this first embodiment of the invention relates to a non-zeolitic substrate based on silica-alumina that contains an amount that is more than 5% by weight and less than or equal to 95% by weight of silica (SiO_2), characterized by:

- a mean pore diameter, measured by mercury porosimetry, encompassed between 20 and 140 Å,
- a total pore volume, measured by mercury porosimetry, encompassed between 0.1 ml/g and 0.6 ml/g,
- a total pore volume, measured by nitrogen porosimetry, encompassed between 0.1 ml/g and 0.6 ml/g,
- a BET specific surface area encompassed between 100 and 550 m^2/g,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 140 Å, of less than 0.1 ml/g,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 160 Å, of less than 0.1 ml/g,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 200 Å, of less than 0.1 ml/g,
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 500 Å, of less than 0.01 ml/g,
- an X diffraction diagram that contains at least the main lines that are characteristic of at least one of the transition aluminas contained in the group that consists of the rho, chi, eta, gamma, kappa, theta and delta aluminas.

The teaching of the US Patent Application of Serial Number 10/696 561 is incorporated here as a reference.

According to a second embodiment of this invention, the substrate of the hydrocracking catalyst comprises at least one silica-alumina, whereby said silica-alumina comprises the following characteristics:

- a content by weight of silica SiO_2 of between 10 and 60%, preferably between 20 and 60%, and even more preferably between 30 and 50% by weight,
- an Na content of less than 300 ppm by weight and preferably less than 200 ppm by weight,
- a total pore volume of between 0.5 and 1.2 ml/g that is measured by mercury porosimetry,
- a specific surface area of more than 200 m^2/g and preferably more than 250 m^2/g, and
- a porosity that is defined as follows:

i) a volume of mesopores whose diameter is between 40 Å and 150 Å, and whose mean diameter varies between 80 and 120 Å representing between 30 and 80% of the total pore volume that is defined above and preferably between 40 and 70%,

ii) a volume of macropores, whose diameter is more than 500 Å and preferably between 1,000 Å and 10,000 Å, represents between 20 and 80% of the total pore volume, preferably between 30 and 60% of the total pore volume, and more preferably, at least 35% of the total pore volume.

According to this invention, the amorphous hydrocracking catalyst comprises palladium and platinum. These two compounds are part of the hydro-dehydrogenating element of the hydrocracking catalyst.

In addition to the palladium and the platinum, the hydro-dehydrogenating element can comprise either one or more noble metals of group VIII of the periodic table, or a combination of at least one metal of group VIB of the periodic table and at least one metal of group VIII.

The hydrocracking catalyst can comprise, in percentage by weight relative to the total mass of the catalyst, 0.2 to 8% by weight, preferably 0.3 to 5% by weight, and more preferably 0.4 to 2% by weight of noble metals of group VIII.

The hydrocracking catalyst can be subjected in advance to a reduction treatment that makes it possible to transform, at least in part, the noble metal oxides into reduced noble metals. One of the preferred methods for carrying out the reduction of the catalyst is a treatment under hydrogen at a temperature of between 150 and 650°C and at a total pressure of between 0.1 and 20 MPa. We also note that any ex-situ reduction method can be suitable.

By way of example, a reduction can include holding at a temperature of 150°C for 2 hours, followed by a rise in temperature up to 350°C at a rate of 1°C per minute, then holding at 350°C for 2 hours. During this reduction treatment, the hydrogen flow rate can be 1,000 liters of hydrogen per liter of catalyst.

According to an essential characteristic of the process of the invention, the hydrocracking stage is implemented at a temperature T2 that is less than hydrorefining temperature T1, whereby the difference between T1 and T2 is between 5 and 50°C, preferably between 10 and 40°C, and more preferably between 15 and 30°C.

The operating conditions that are used during the hydrocracking stage of the process according to the invention can be:

- a temperature T2 that is more than 200°C, preferably between 250 and 420°C, more preferably between 300 and 400°C, even more preferably between 330 and 380°C;
- a pressure of more than 7.5, preferably more than 8.2 MPa, more preferably more than 9.0 MPa, and even more preferably more than 11.0 MPa and less than 20 MPa;
- a volumetric flow rate of between 0.1 and 20 h-1, preferably between 0.1 and 6 h-1, and more preferably between 0.2 and 3h-1;
- an amount of hydrogen that is introduced such that the volumetric ratio of liters of hydrogen per liter of hydrocarbon is between 80 and 5,000 l/l, preferably between 100 and 2,000 l/l.

These operating conditions that are used during the hydrocracking stage can be established so as to reach one conversion per pass into products that have a boiling point of less than 340°C (and, even better, less than 370°C) and more than 30% by weight, preferably between 40 and 95% by weight.

The effluent that is recovered during the hydrocracking stage is generally subjected to a so-called final separation stage so as to separate the gases, such as ammonia, hydrogen sulfide, hydrogen, as well as the other light gases of the effluent.

Following this final separation stage, an atmospheric distillation can be implemented. In some cases, this atmospheric distillation is completed by a vacuum distillation. The distillation has as its object to carry out the separation between the converted products, i.e., generally having boiling points of less than 340°C (and, even better, less than 370°C) and an unconverted liquid fraction.

It is advantageously possible to distill at atmospheric pressure to obtain several converted fractions, such as, for example, gasolines, kerosene, gas oil and an unconverted liquid fraction having an initial boiling point that is more than 340°C or else more than 370°C.

To improve the final separation, it is possible to add a vacuum distillation. This will be the case, for example, for distilling the diesel with better effectiveness.

The unconverted liquid fraction can be completely or partially injected into the hydrocracking reactor so as to be converted there.

Advantageously, the final separation is carried out with separation stage means implemented between the hydrorefining and hydrocracking stages when the latter comprise an atmospheric distribution and optionally a vacuum distillation.

This process makes it possible to obtain levels of conversion of the feedstock into products whose boiling point is less than 370°C, more than 70% and preferably more than 80%. This process also makes it possible to obtain high selectivities of middle distillates and more especially of gas oil.

The gas oil and the kerosene that are obtained exhibit excellent qualities, i.e., a high cetane number and a low sulfur content.

The examples below illustrate this invention without, however, limiting its scope.

Example 1: Preparation of a Hydrocracking Catalyst According to the Invention (C1)

The preparation of substrate S1 according to the invention is described below.

The silica-alumina gels are prepared by mixing soda silicate and water, by sending this mixture into an ion exchange resin. A solution of aluminum hexahydrate in water is added to the decationized silica sol. So as to obtain a gel, ammonia is added, then the precipitate is filtered, and washing is carried out with a solution of water and concentrated ammonia until the conductivity of the wash water is constant. The gel that is obtained from this stage is mixed with Pural boehmite powder such that the final composition of the mixed substrate of anhydrous product is, at this stage of the synthesis, equal to 60% Al_2O_3-40% SiO_2. This suspension is passed into a colloidal mill in the presence of nitric acid. The content of added nitric acid is adjusted such that the percentage at the nitric acid mill outlet is 8% relative to the mass of solid mixed oxide. This mixture is then filtered so as to reduce the amount of water of the mixed cake. Then, the cake is mixed in the presence of 10% nitric acid and then extruded. The mixing is done in a Z-arm mixing machine. The extrusion is carried out by passage of the paste through a die that is equipped with orifices that are 1.4 mm in diameter. The extrudates that are thus obtained are dried at 150°C and then calcined at 550°, and then calcined at 700°C in the presence of water vapor.

The characteristics of the S1 substrate are as follows:

- a composition of the silica-alumina substrate of 60.7% Al_2O_3 and 39.3% SiO_2;
- a BET surface area of 258 m^2/g;

- a total pore volume, measured by nitrogen adsorption, of 0.47 ml/g;
- a mean pore diameter, measured by mercury porosimetry, of 69 Å;
- a ratio between volume V2, measured by mercury porosimetry, encompassed between D_{mean} – 30 Å and D_{mean} + 30 Å to the total mercury volume of 0.89;
- a volume V3, measured by mercury porosimetry, encompassed in the pores with a diameter of more than D_{mean} + 30 Å of 0.032 ml/g;
- a volume V6, measured by mercury porosimetry, encompassed in the pores with a diameter of more than D_{mean} + 15 Å of 0.041 ml/g;
- a ratio between the adsorption surface area and the BET surface area of 0.83;
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 140 Å of 0.012 ml/g;
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 160 Å of 0.0082 ml/g;
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 200 Å of 0.0063 ml/g;
- a pore volume, measured by mercury porosimetry, encompassed in the pores with a diameter of more than 500 Å of 0.001 ml/g;
- an X diffraction diagram that contains at least the gamma characteristic main lines and the peaks at one d encompassed between 1.39 and 1.40 Å and the peaks at one d encompassed between 1.97 Å and 2.00 Å, whereby the X diffraction diagram also contains the characteristic main lines of

gamma-alumina and in particular the peaks at one d encompassed between 1.39 and 1.40 Å and the peaks at one d encompassed between 1.97 Å and 2.00 Å;

- an atomic sodium content of 200 +/-20 ppm;
- an atomic sulfur content of 800 ppm; and
- NMR MAS spectra of the solid of ^{27}Al of the catalysts that show two clusters of separate peaks, a first type of aluminum whose maximum resonates toward 10 ppm that extends between –100 and 20 ppm, the position of the maximum suggesting that these radicals are essentially of Al_{VI} type (octahedral), a second type of minority aluminum whose maximum resonates toward 60 ppm and that extends between 20 and 100 ppm, whereby this cluster can be decomposed into at least two radicals, and the predominant radical of this cluster would correspond to Al_{IV} atoms (tetrahedral), whereby the proportion of octahedral Al_{VI} is 70%.

The catalyst contains a single silico-aluminum zone with an Si/Al ratio that is determined by a MET microprobe of 0.63.

Catalyst C1 is obtained by impregnation in the dry state of substrate S1 by an aqueous solution that contains platinum and palladium salts. The platinum salt is hexachloroplatinic acid $H_2PtCl_6*6H_2O$, and the palladium salt is the palladium nitrate $Pd(NO_3)_2$. After maturation at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried at 120°C for one night and then calcined at 500°C under dry air. The final content of Pt is 0.5% by weight. The final content of Pd is 1.0% by weight.

Example 2: Preparation of a Hydrocracking Catalyst According to the Invention (C2)

Substrate S2 is an amorphous silica-alumina that has a chemical composition of 40% by weight of SiO_2 and 60% by weight of Al_2O_3. Its Si/Al molar ratio is 0.56. Its Na content is on the order of 100-120 ppm by weight. It is in the form of cylindrical extrudates with a diameter of 1.7 mm. Its specific surface area is 320 m^2/g. Its total pore volume, measured by mercury porosimetry, is 0.83 ml/g. The pore distribution is bimodal. In the field of mesopores, we observe a wide peak of between 40 and 150 Å with a dV/dD maximum toward 70 Å. On the substrate, macropores that are larger than 500 Å in size represent about 40% of the total pore volume.

Catalyst C2 is obtained by impregnation in the dry state of substrate S2 by an aqueous solution that contains platinum and palladium salts. The platinum salt is hexachloroplatinic acid $H_2PtCl_6*6H_2O$, and the palladium salt is the palladium nitrate $Pd(NO_3)_2$. After maturation at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried at 120°C for one night and then calcined at 500°C in dry air. The final content of Pt is 0.5% by weight. The final content of Pd is 1.0% by weight.

Example 3: Evaluation of C1 and C2 Catalysts Under Conditions According to the Invention

A vacuum distillate is subjected to a hydrorefining stage on an HR448 catalyst that is marketed by Procatalyse, with a base of nickel (3.3% by weight), molybdenum (16.5% by weight) supported on alumina, in the presence of hydrogen, at a temperature

of 385°C and at an hourly volumetric flow rate of 0.50 h^{-1}. During this hydrorefining stage, the conversion into products whose boiling point is less than 370°C is about 35% by weight.

The effluent that is produced during this hydrorefining stage is subjected to a separation stage that makes it possible to recover a 370°C+ fraction that is subjected to a hydrocracking stage.

The physico-chemical characteristics of the 370+ fraction that is subjected to the hydrocracking stage are described in Table 1:

Table 1: Characteristics of the Fraction that is Subjected to the Hydrocracking Stage.

Density (20/4)	0.854
Organic Sulfur (ppm by weight)	8
Organic Nitrogen (ppm by weight)	2
H2S (ppm by weight)	5
NH3 (ppm by weight)	4
Simulated Distillation	
Starting Point	325°C
5% Point	366°C
10% Point	384°C
50% Point	449°C
90% Point	527°C
End Point	591°C

The fraction that is subjected to the hydrocracking stage is introduced into a hydrocracking test unit that simulates the operation of the second stage of a 2-stage hydrocracking process that comprises a fixed-bed reactor with upward circulation of the feedstock ("up flow") into which 50 ml of catalyst is introduced.

Catalysts C1 and C2 are reduced in advance at 350°C for 2 hours under a hydrogen flow rate of 50 l/h, under a total pressure of 14 MPa. At the beginning of this reduction stage, the temperature is increased to 350°C with a rate of temperature rise of 1°C per minute.

Once the reduction is carried out, the fraction that is described in Table 1 is then hydrocracked. The operating conditions of this test simulating the second stage of the 2-stage hydrocracking process are as follows:

Table 2: Operating Conditions

Total Pressure	14 MPa
Catalyst	50 ml
Temperature	365 – 370 - 375°C
Hydrogen Flow Rate	50 l/h
Feedstock Flow Rate	50 ml/h

The catalytic performance levels are expressed by the net conversion into products that have a boiling point of less than 370°C, by the coarse selectivity of middle distillate (fraction 150-370°C) and by the ratio between the gas oil yield and the kerosene yield in the middle distillate fraction. They are expressed starting from the simulated

distillation results. These performance levels are determined at different temperature levels of the test. For each temperature level, the performance levels are measured on the catalyst after a stabilization period, generally at least 72 hours, has elapsed.

Net conversion CN is provided by the following formula:

$CN\ 370^{-} = [(\%\ 370^{-}_{effluents}) - (\%\ 370^{-}_{feedstock})]/[100 - (\%\ 370^{-}_{feedstock})]$ with:

$\%\ 370^{-}_{effluents}$: content by mass of compounds that have boiling points of less than 370°C in the effluents, and

$(\%\ 370^{-}_{feedstock}$: content by mass of compounds that have boiling points of less than 370°C in the feedstock.

Middle distillate coarse selectivity SB is obtained as follows:

$SB_{middle\ distillates} = [(fraction\ (150°C - 370°C)_{effluents})]/[(\%\ 370°C^{-}_{effluents})]$

The ratio between the gas oil yield and the kerosene yield (gas oil/kerosene ratio) in the middle distillate fraction corresponds to the ratio between the yield of the fraction (250°C - 370°C) of the effluent and the yield of the fraction (150°C - 250°C) of the effluent.

The catalytic performance levels that are obtained on the C1 and C2 catalysts are provided in Table 3 below.

Table 3: Catalytic Results that are Obtained on Catalysts C1 and C2.

Catalyst	Temperature (°C)	CN 370°C – (% by Weight)	Middle Distillate SB (% by Weight)	Gas Oil/Kerosene Ratio (% by Weight/% by Weight)
C1	360	60	77	1.4
C1	370	80	71	1.0
C1	375	90	68	0.7
C2	360	59	75	1.3
C2	370	78	70	0.9
C2	375	89	67	0.6

The C1 and C2 amorphous acid hydrocracking catalysts that are used in the hydrocracking stage make it possible to obtain high levels of conversion into products that have a boiling point of less than 370°C and high selectivities of middle distillates, whereby they do so at temperature levels such that the temperature of the hydrocracking stage is less than the temperature of the hydrorefining stage by 10 to 25°C, whereby the hydrorefining stage is carried out at 385°C in this example.

The effluent that is obtained from the hydrocracking undergoes a distillation so as to recover the kerosene fraction (compounds that have boiling points of more than 150°C and less than 250°C) and the gas oil fraction (compounds that have boiling points of more than 250°C and less than 370°C). The kerosene and gas oil fractions are then analyzed.

The characteristics of these fractions are combined in Table 4 regarding kerosene and in Table 5 regarding gas oil.

Table 4: Characteristics of the Kerosene Fraction that is Obtained

Catalyst	Smoke Point (mm)
C1	27
C2	26

Table 5: Characteristics of the Gas Oil Fraction that is Obtained

Catalyst	Sulfur Content (ppm by Weight)	Engine Cetane	Content of Aromatic Compounds (% by Weight)	Content of Polyaromatic Compounds (% by Weight)
C1	7	57	9.1	1.7
C2	8	56	9.3	1.9

The C1 and C2 amorphous acid hydrocracking catalysts of the PtPd/silica-alumina type according to the invention, used in the second hydrocracking stage of the hydrocracking process according to the invention, make it possible to obtain kerosene and gas oil fractions of excellent quality.

Example 5: Evaluation of the C1 Catalyst Under Conditions that are Not in Accordance with the Invention

Catalyst C1 is evaluated under hydrocracking conditions.

The fraction that is subjected to the hydrocracking is identical to the one that is described in Example 3 whose characteristics are transferred into Table 1.

Before this fraction is injected, catalyst C1 undergoes a reduction treatment under operating conditions that are identical to the operating conditions of the reduction treatment described in Example 3.

Once the reduction is made, the fraction that is described in Table 1 can be treated. The operating conditions of this test, not in accordance with the invention, are described in Table 8. The temperature of the hydrocracking stage is equal to the temperature of the hydrorefining stage, or 385°C.

Table 8: Operating Conditions

Total Pressure	14 MPa
Catalyst	50 ml
Temperature	385°C
Hydrogen Flow Rate	50 l/h
Feedstock Flow Rate	50 ml/h

The catalytic performance levels that are obtained on catalyst C1 under these operating conditions are provided in Table 9 below.

Table 9: Catalytic Results that are Obtained on Catalyst C1.

Catalyst	Temperature (°C)	CN 370° - (% by Weight)	Middle Distillate SB (% by Weight)	Gas Oil/Kerosene Ratio (% by Weight/% by Weight)
C1	385	100	49	0.6

The conversion into products that have a boiling point of less than 370°C is total, but the selectivity of middle distillates (150-370°C) is very low.